INTERFERENCE FILTER HAVING A GLASS SUBSTRATE

Substrates that demand high expansion with good chemical durability are often manufactured from optical glasses. Optical glasses may be employed in various applications, such as substrates for thin-film interference filters used in fiber optic systems. Generally, these interference filters are fabricated from multiple layers of conducting and insulating materials or films that together result in a filter that passes only a narrow bandwidth of incident radiation. Such filters are described, for example, in *Optical Filter Design and Analysis-A Signal Processing Approach* by Christie K. Madsen and Jian H. Zhao published by John Wiley & Sons, 1999.

In one particular application, there is a strong demand for a glass substrate capable of being incorporated into an interference filter for wavelength division multiplexing (WDM) or dense wavelength division multiplexing (DWDM) applications. Thin-film interference filters for WDM and DWDM applications have high requirements in terms of the narrow bandwidth of light transmittal (*Introduction to DWDM Technology* by Stamatios V. Kartalopoulos, published by IEEE Press, 2000). Such bandwidths are expressed as a width in passed frequency, typically 200GHz, 100GHz, 50GHz, or less, with smaller values indicating a narrower bandwidth of transmission. For example, a 100GHz filter within the 1.5μm telecommunications band corresponds to a wavelength spread of 0.8nm; and, a 50GHz filter within the same 1.5μm telecommunications band corresponds to a wavelength spread of 0.4nm. These filters preferably have bandwidths of less than 200GHz pass frequency in the 1.5μm wavelength region. An optical designer can fabricate useful telecommunications modules using such filters. For example, an optical demultiplexer can be constructed using a multitude of such thin-film interference filters, each one of which separates out a particular wavelength of interest.

Most desirably, the substrate is characterized by high transmission in the near IR where DWDM systems operate, *i.e.*, wavelengths at or near 1.5 μm, a refractive index value at 587.6 nm, n_d, of between 1.50 and 1.70, and a high transformation temperature, T_g, exceeding 350 °C, most preferably exceeding 400 °C. High transmission at 1.5μm is characterized by a value of digital transmittance, including Fresnel reflection loss, exceeding 88%, more preferably equivalent to or exceeding

90% at 1.5μm through a 1.0 mm thickness. Preferably, these filters have minimal wavelength drift with change in temperature. Glass substrates with high thermal expansion, CTE, and high values of Young's modulus, E, allow for decreased amounts of thermally-induced drift ($d\lambda/dT$) in the transmission wavelengths of interest, e.g., 1450 - 1620 nm, 1480 - 1620 nm, and 1450 - 1550 nm. A particularly desirable range of thermal expansion values is from 90 to 140 x 10^{-7}/°C, particularly 110 to 140 x 10^{-7}/°C, over a temperature range of -30°C to +70°C coupled with a Young's modulus >80 GPa. More preferably, the thermal expansion should lie in the range of 100 to 130 x 10^{-7}/°C over the same temperature range in combination with a Young's modulus value >85 GPa.

Such narrow bandwidths are highly demanding and difficult to achieve and push the limits of available coating technology. Consequently, the substrate properties are becoming more demanding, and the advanced coating industry desires to have new substrate glasses available that offer enhanced or optimized properties for applications at less than 200GHz bandwidth range.

Thus, a desired embodiment of the invention is a glass making available an interference filter for a fiber optic system including a substrate and a film coating the substrate. Typically, the substrate is coated with a series of layers of differing materials having properties, e.g., indices of refraction, producing interference effects achieving the desired wavelength transmission spectrum. Fiber optic systems comprise one or more light sources, fiber optic transmission components, filters and end use components, e.g., detection, amplifiers, etc. Glasses of the invention and their properties are described in the following tables:

TABLE 1

Composition (mol%) and Properties		
Oxide/Property	Preferred	Most Preferred
SiO_2	35 – 75	40 – 70
GeO_2	0 – 10	0-5
B_2O_3	0 – 8	0 – 5
Al_2O_3	0 – 8	0 - 5
Li_2O	>0 – 25	>0 – 25
Na_2O	0 – 60	0 – 35
K_2O	0 – 6	0 – 5
MgO	0 – 35	0 – 25
Σ BaO, SrO, CaO, ZnO, PbO	0 – 10	0 – 5
TiO_2	0 – 5	0 – 3
La_2O_3	0 – 30	0 – 12
RE_2O_3	0 – 12	0 – 10
Y_2O_3	> 0 – 30	>0 – 25
As_2O_3	0 – 0.5	0 – 0.3
F	0 – 5	0 – 3
Sum R_2O_3, R=Al, B, La and RE	0 – 40	0 – 40
n_d	>1.5	1.50 – 1.70, especially 1.50 - 1.65
T (%) at 1550 nm for 1 mm	> 88	> 90
$CTE_{-30/+70}[x10^{-7}/C]$	≥90, especially ≥110	>100, especially >110
Tg [C]	≥350C	≥400C
E [GPa]	>80	>85

TABLE 2

Composition (mol%) and Properties		
SiO_2	40-60	
GeO_2	0-10	
B_2O_3	0-10	
Al_2O_3	0-4	
Li_2O	>0-26	
Na_2O	>0-26	
K_2O	0-15	
MgO	0-15	
$\sum$ BaO, SrO, CaO, ZnO, PbO	0-10	
TiO_2	0-9	
ZrO2	0-2	
La_2O_3	0-4	
RE_2O_3	0-4	
Y_2O_3	>0-5	
Sc_2O_3	0-4	
Nb_2O_5	0-2	
F	0-5	
$\sum R_2O_3$, R=Al, B, La and RE	0-25	
As_2O_3	0-0.5	
Oxide/Property	**Preferred**	
n_d	>1.5	
T (%) at 1550 nm for 1 mm	>88	
$CTE_{-30/+70}[x10^{-7}/C]$	≥90	
Tg [C]	≥350	
E [Gpa]	>80	

TABLE 3

Composition (mol%) and Properties		
SiO_2 45.0-58.0%		
B_2O_3 0.0-5.0%		
Al_2O_3 0.0-3.0%		
Li_2O 6.5-16.5%		
Na_2O 7.0-24.0%		
K_2O 0.0-12.0%		
MgO 0.0-8.0%		
CaO 0.0-8.0%		
SrO 0.0-8.0%		
BaO 0.0-8.0%		
TiO_2 0.0-12.0%		
ZrO_2 0.5-5.5%		
Ta_2O_5 0.0-1.0%		
Gd_2O_3 + La_2O_3 + Y_2O_3 2.70-3.30%		
As_2O_3 0.0-0.15%		
Oxide/Property	**Preferred**	**Most Preferred**
n_d	>1.5	1.50 - 1.70
T (%) at 1550 nm for 1 mm	>88	>90
$CTE_{-30/+70}[x10^{-7}/C]$	$\geq$90	>100
Tg [C]	400-485	420-480
E [Gpa]	>80	>85

TABLE 4

Composition (mol%) and Properties		
SiO_2 45.0-58.0%		
B_2O_3 0.0-5.0%		
Li_2O 6.5-16.5%		
Na_2O 7.0-24.0%		
K_2O 0.0-12.0%		
MgO 0.0-8.0%		
CaO 0.0-8.0%		
SrO 0.0-8.0%		
BaO 0.0-8.0%		
TiO_2 0.0-12.0%		
ZrO_2 0.5-5.5%		
Ta_2O_5 0.0-1.0%		
Gd_2O_3 + La_2O_3 2.70-3.30%		
As_2O_3 0.0-0.15%		
Oxide/Property	**Preferred**	**Most Preferred**
n_d	>1.5	1.50 - 1.70
T (%) at 1550 nm for 1 mm	>88	>90
$CTE_{-30/+70}[x10^{-7}/C]$	≥ 90	>100
Tg [C]	400-485	420-480
E [Gpa]	>80	>85

RE = rare earth ions, excluding La, that do not impart unacceptable absorption at the wavelength of interest (e.g., 1450 - 1550 nm, especially 1480-1620 nm), i.e., do not degrade T overall beyond the numbers given above. As a more preferred example of acceptable absorption, RE allows for an internal transmission of > 0.99 for a 1 mm thickness sample, thereby allowing for an insertion loss of < 0.9 dB. Nd and Ho are non-limiting examples of rare earth ions that may be used in the current application.

Without being bound by theory, it is believed that the individual components of the glasses affect certain properties. It is believed that in glasses of the present invention SiO_2 and GeO_2, both are network formers and Y_2O_3 and La_2O_3 are intermediates that do participate as network formers. Na_2O is a network modifier that typically affects index, expansion, and transformation temperature. Li_2O is a network modifier that affects index expansion, transformation temperature, Young's modulus, and thermal conductivity. MgO is a network modifier that affects index, expansion, transformation temperature, Young's modulus, and thermal conductivity. Sc_2O_3 and other rare earth oxides in the prescribed amounts can be directly substituted for Y_2O_3 and La_2O_3. The addition of TiO_2 and/or ZrO_2 to the glass helps maintain durability.

Expansion and Young's modulus are properties that are normally inversely proportional to each other in glasses in that as one property is raised through compositional adjustments, the other is lowered (*Glass*, by Horst Scholze,1991, published by Springer-Verlag). Surprisingly, the introduction of Li_2O and/or MgO in glasses of the present invention causes the above properties to become proportional to each other so that both can be raised together as needed to produce a stable glass substrate with the required properties of high expansion and high Young's modulus.

The substrates of the present invention may be made by conventional glass melting techniques. Raw materials can be melted in platinum crucibles and held at temperatures around 1400°C for up to five hours.

The interference filter for a fiber optic system also includes at least one film desirably in the form of a layer. Such films can be selected from SiO_2, Ta_2O_5, HfO_2,

etc. These can be applied by commercially available standard ion beam deposition systems such as the SPECTOR® system available from Ion Tech, Inc. of Fort Collins, Colorado, or the Advanced Plasma Source 1104 System from Leybold Optics of Hanau, Germany. In addition to being particularly useful for DWDM filters, these glasses are also exceptionally useful as high expansion glasses for fabrication of hybrid structures that demand a high expansion glass with good chemical durability, *e.g.*, for the purposes of longwave pass filters, polarizing components, band pass filters, etc.

Preferred embodiments also include a glass comprising:

Oxide	**Mole %**
SiO_2	45-55
GeO_2	0-5
B_2O_3	0-8
Al_2O_3	0-2
Li_2O	>0-17
Na_2O	>0-19
K_2O	0-6
MgO	0-13
Σ BaO, SrO, CaO, ZnO, PbO	0-5
TiO_2	0-5
ZrO_2	0-1
La_2O_3	0-3
RE_2O_3	0-3
Y_2O_3	>0-4.5
Sc_2O_3	0-3
Nb_2O_5	0-1
F	0-3
Σ R_2O_3, R=Al, B, La, and RE	0-15
As_2O_3	0-0.3

and the above glass preferably having the following properties:

Property	Range
n_d	1.50-1.70
T(%) at 1550 nm for 1.0 mm	> 90
CTE (-30 to +70°C) x $10^{-7}/^{0}C$	≥ 100
Tg (°C)	≥ 400
E [GPa]	> 85

as well as glass comprising:

Oxide	Mole %
SiO_2	46.0-52.0
B_2O_3	0.0-1.0
Al_2O_3	0.0-1.5
Li_2O	7.0-16.0
Na_2O	7.0-20.0
K_2O	4.0-12.0
MgO	0.0-7.5
CaO	0.0-7.5
SrO	0.0-7.5
BaO	0.0-7.5
TiO_2	1.0-10.5
ZrO_2	1.5-5.0
Ta_2O_5	0.3-0.7
La_2O_3 + Gd_2O_3 + Y_2O_3	2.6-2.9
As_2O_3	0.0-0.15

the above glass preferably having the following properties:

Property	**Range**
n_d	**1.50 - 1.70**
T(%) at 1550 nm for 1.0 mm	**>88**
CTE (-30 to +70°C) x $10^{-7}/^{0}C$	**>100**
Tg (°C)	**415-480**
E [GPa]	**>80**

and a glass comprising:

Oxide	Mole %
SiO_2	46.0-52.0
B_2O_3	0.0-1.0
Li_2O	7.0-16.0
Na_2O	15.5-20.0
K_2O	4.0-5.5
MgO	0.0-7.5
CaO	0.0-7.5
SrO	0.0-7.5
BaO	0.0-7.5
TiO_2	1.0-10.5
ZrO_2	2.5-5.0
Ta_2O_5	0.3-0.7
La_2O_3 + Gd_2O_3	2.7-2.8
As_2O_3	0.0-0.15

the above glass preferably having the following properties:

Property	**Range**
n_d	**1.50 - 1.70**
T(%) at 1550 nm for 1.0 mm	**>88**
CTE (-30 to +70°C) x 10^{-7}/°C	**>100**
Tg (°C)	**415-480**
E [GPa]	**>80**

Preferred embodiments also include an interference filter comprising a glass substrate having at least two interference layers coated thereon, wherein the glass substrate comprises one of the compositional spaces above.

Preferred embodiments also include a fiber optic system comprising a light source, a fiber optic transmission component, a receiver of transmitted radiation and an interference filter comprising a glass substrate having at least two interference layers coated thereon, said glass substrate comprising one of the glass spaces above.

Moreover, preferred embodiments include a process for making glasses according to the invention comprising melting raw materials corresponding to oxides in the glass, refining a resultant glass melt, casting the melt in a mold and optionally

annealing, or casting into a mold a glass melt produced from raw materials corresponding to oxides in the glass.

Additionally, preferred embodiments include a demultiplexing optical component comprising the above interference filter and a method of demultiplexing, comprising passing an optical signal of multiple wavelengths through a demultiplexing optical component above, whereby one or more wavelengths of interest are separated.

Finally, preferred embodiments include a process for making an interference filter comprising coating any glass described above.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

In the foregoing and in the following example, all temperatures are set forth uncorrected in degrees Celsius; and, unless otherwise indicated, all parts and percentages are by mole.

The entire disclosures of all applications, patents and publications, cited above or below including provisional applications number 60/259,706 filed January 5, 2001, and 60/317,493 filed September 7, 2001, are hereby incorporated by reference.

Examples

The glasses in the Tables below were prepared as follows. Chemical compounds were weighed in the proper amounts to produce the desired composition and melted within a platinum crucible at temperatures in excess of 1300°C to produce vitrified material. Once this batch melting was complete, the glass melt was stirred and refined at temperatures up to 1500°C for several hours prior to casting the molten glass into a steel mold. Cast glasses were annealed at temperatures between 420 and 500 °C for two hours before being cooled to room temperature at a cooling rate of 10°C/hr. to 40°C/hr.

Table 4

Oxide Mole%	1 (Comparative)	2	3	4	5
SiO_2	69.93	59.93	54.93	54.01	49.10
Li_2O		10.00	10.00	9.83	9.83
Na_2O	24.98	24.98	24.98	24.56	24.57
MgO			5.00	4.91	9.83
Y_2O_3	4.99	4.99	4.99	4.91	4.91
F				1.68	1.66
As_2O_3	0.10	0.10	0.10	0.10	0.10

The glass castings produced were next cut to yield characterization samples with the following property results:

Table 5

Property	Value	1 (Comparative)	2	3	4	5
n_d	>1.5	1.54	1.56	1.56	1.56	1.57
CTE -30/+70 x $10^{-7}/^{o}C$	$\geq$90	99	113	113	114	114
T(%) at 1550 nm for 1.0 mm	>88	92.1	91.2	91.4	91.4	91.4
Tg (°C)	$\geq$350	600	474	449	438	431
E (GPa)	>80	74	83	85	86	89

Based on these measured properties, glasses of the invention are clearly useful as improved substrate glasses for filtering applications.

Additional properties of these glasses have been determined. These are detailed below in Table 6. The coefficient of thermal expansion was measured using push-rod dilatometric methods over -30 to +70 °C with a rate of change of 1.5 °C/min. The digital percent (total) transmittance was measured at 1.5 μm (thickness 1.0 mm) using a Perkin-Elmer Lambda 9 spectrophotometer. The refractive index and Vd (Abbe number) were measured using a v-block refractometer in accordance with Journal of Scientific Instruments 18 234 (1941). Youngs modulus and Poisson ratio were determined by utilizing a Matec Pulse Echo Overlap System model 6000, or a J.W. Lemmens GrindoSonic Impulse Excitation Technique Instrument Model MK5 "Industrial". Thermal conductivity was measured using a Dynatech C-Matic Thermal Conductance Tester model TCHM-DV. T_g was measured using either a Harrop Laboratories Dilatometer Model AT-710 or a Theta Industries Dilatometer Model 1200C.

Table 6

Property	1 (Comparative)	2	3	4	5
n_F-n_C	0.009108	0.010483	0.010642	0.010568	0.010843
V_d	59.13	53.15	52.98	53.17	52.43
Density g/cm^3	2.71	2.75	2.78	2.78	2.81
CTE 20-300 x 10^{-7}/^{0}C	110	135	137	138	138
Poisson's Ratio	0.231	0.247	0.249	0.248	0.255

Table 7

Oxide Mole%	6 (comparative)	7	8	9	10
SiO_2	69.93	49.10	59.93	49.10	44.10
Li_2O		25.80	10.00	9.83	9.83
Na_2O	24.98	8.60	24.98	24.57	24.57
MgO		9.83		9.83	9.83
Y_2O_3	4.99	4.91	4.99	4.91	4.91
F		1.66		1.66	1.66
TiO_2					5.00
As_2O_3	0.10	0.10	0.10	0.10	0.10

The glass castings produced were next cut to yield characterization samples with the following property results:

Table 8

Property	Value	6 (comparative)	7	8	9	10
n_d	> 1.5	1.54	1.59	1.56	1.57	1.60
CTEx10^{-7}/K (-30 to +70)	$\geq$90	99	101	113.5	113	115
T(%) at 1550 nm for 1.0 mm	>88	92.1	91.0	91.2	91.4	90.8
T_g (^{0}C)	≥ 350	600	438	474	431	451
E (GPa)	> 80	74	101.5	83	90	93

Based on these measured properties, glasses of the invention are clearly useful as improved substrate glasses for filtering applications.

Additional properties of these glasses have been determined, as above. These are detailed below in Table 9.

Table 9

Property	6 (comparative)	7	8	9	10
n_F-n_C	0.009108	0.010859	0.010483	0.010843	0.013548
V_d	59.13	54.50	53.15	52.43	44.64
density (g/cm^3)	2.71	2.80	2.76	2.81	2.89
CTE x 10^{-7}/K (20-300)	110	126	135	138	140
Thermal Conductivity (W/mK) 25^{0}C 90^{0}C	0.881 0.912	1.14 1.21	0.893 0.926	0.981 1.04	1.01 1.07
Poisson's Ratio	0.23	0.26	0.25	0.26	0.25

Table 10

Oxide Mole%	11	12	13	14	15
SiO_2	54.46	51.56	51.56	48.90	47.12
B_2O_3	0.52	0.44	0.45	0.0	0.0
Li_2O	7.34	7.57	7.56	12.90	13.78
Na_2O	20.69	18.90	18.90	18.89	18.89
K_2O	4.19	4.89	4.89	4.89	4.45
MgO	4.20	7.12	7.12	0.0	0.0
CaO	4.20	0.0	0.0	0.0	0.0
SrO	0.0	0.0	0.0	0.0	0.0
BaO	0.0	0.0	0.0	0.0	0.0
TiO_2	0.0	3.56	3.55	8.44	8.89
ZrO_2	0.53	2.67	2.67	2.66	3.56
Ta_2O_5	0.52	0.44	0.44	0.45	0.45
La_2O_3	3.25	2.67	0.0	0.0	0.0
Gd_2O_3	0.0	0.0	2.67	2.76	2.76
As_2O_3	0.11	0.11	0.11	0.11	0.11

The glass castings produced were next cut to yield characterization samples with the following property results:

Table 11

Property	Value	11	12	13	14	15
CTE-30/+70 X10-7/C	$\geq$90	115.8	109.1	106.5	114.0	113.3
Tg C	400-485	419	443	456	452	453
nd	>1.5	1.57637	1.59731	1.59388	1.62656	1.63745
T(%) at 1550 nm for 1.0 mm	>88	91.7	90.9	91.0	90.1	89.9
Youngs Modulus [GPa]	>80	82.2	84.4	85.7	88.3	90.1

Based on these measured properties, glasses of the invention are clearly useful as improved substrate glasses for filtering applications.

Additional properties of these glasses have been determined, as above. These are detailed below in Table 12.

Table 12

Property	11	12	13	14	15
Abbe number	51.81	46.72	47.08	41.91	40.87

Table 13

Oxide Mole%	16	17	18
SiO_2	47.17	47.17	49.17
B_2O_3			
Al_2O_3			1.0
Li_2O	10.80	10.80	7.80
Na_2O	15.92	13.92	7.92
K_2O	4.45	4.45	10.45
MgO	3.00	3.00	
CaO			4.00
SrO		2.00	6.00
BaO	6.00	6.00	6.00
ZnO			
TiO_2	7.40	7.40	2.40
ZrO_2	2.06	2.06	2.06
Ta_2O_3	0.45	0.45	0.45
La_2O_3			
Gd_2O_3			
Y_2O_3	2.76	2.76	2.76
Total	100.1	100.1	100.1

The glass casting produced were next to yield characterization samples with the following property results.

Table 14

Property	16	17	18
CTE-30/+70	108.1	103.4	
X10-7/C			
T_g C	452	462	
nd	1.63390	1.64000	
ABBE NUMBER 40 C/hr	42.70	42.78	
DENSITY gm/cm3	3.11	3.15	
T% at 1550 mm for 1nm	90.4	90.0	
E Gpa	88.8	92.7	

The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding example.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention and, without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.